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ADSORPTION OF ODOROUS POLLUTANTS BY ACTIVE MANGANESE DIOXIDE

D. F. S. Natusch, et al

Illinois University

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16. ABSTRACT The report gives results of an investigation of the adsorption of odorous pollutants by active manganese dioxide (MnO_2). Hydrogen sulfide (H_2S), mercaptans, and an amine were adsorbed in a fixed bed of active MnO_2 (impregnated on sawdust) and several activated carbons. Pollutant removal efficiencies were measured as functions of H_2S concentration, flow rate, particle size, relative humidity (RH), and bed depth. The outlet concentration of H_2S from the MnO_2-sawdust bed is considerably below that from an activated charcoal bed of the same volume and at the same conditions, often by more than an order of magnitude. The useful capacity of the MnO_2-sawdust bed can be greater than 4 times that of activated carbon. The efficiency of MnO_2-sawdust is maximum at 80% RH. Both MnO_2-sawdust and activated carbon are inefficient at below 20% RH. The MnO_2-sawdust bed acts catalytically when mercaptans and air are passed through it at room temperature: the disulfide is formed and there is no decrease in bed efficiency with time. Amines are adsorbed by the filter at an efficiency less than with activated carbon. Fundamental studies of the MnO_2-sawdust were carried out and preliminary correlations were made between bed efficiency and capacity and filter characteristics such as surface area, percent Mn, K, Na, and C, and the Mn valence state.

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Odor Control	Amines	Stationary Sources	05E
Deodorizing	Activated Carbon	Mercaptans	07A, 11G
Manganese Oxides		Activated Manganese Dioxide	07B
Adsorption			
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by

D.F.S. Natusch, J.L. Hudson, R.L. Solomon,
R. Tanner, and A. Miguel

School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

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EPA Project Officer: Belur N. Murthy

Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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I: INTRODUCTION

In this report we discuss the adsorption of pollutants such as H_2S, mercaptans, and amines on a solid filter which is a manganese oxide deposited on the surface of wood sawdust. The work was carried out in the one year period June 15, 1972, to June 15, 1973.

The filter is prepared by reaction of $KMnO_4$ with the sawdust. For convenience, the oxide is denoted by MnO_2 although its exact form has not yet been determined. Its performance is also compared to several commercially available activated carbons. For H_2S, both the efficiency and capacity of the MnO_2-sawdust are superior to those of all activated carbons tested. The influence of a number of operating parameters on odor removal efficiency and capacity was determined. Some data correlation has been made with a view toward possible use in preliminary system design and/or scale-up, and fundamental studies on the filter material were made. A standard preparation of MnO_2-sawdust was employed and its performance assessed as a function of odor concentration (0.4-200 ppm for H_2S), relative humidity (8%-90%), flow rate (20-600 ft/min),* bed depth (1-3 inches)* and particle size (4-6, 6-8, 8-10 and 10-14 mesh, Tyler). Hemlock and fir sawdusts were employed and limited studies were carried out with the ground hard inner ring of corn cobs.

II. EXPERIMENTAL METHOD

A. Apparatus

The MnO_2-sawdust or activated carbon to be tested was held in a bed through which an air pollutant mixture was drawn by a vacuum pump. The desired concentration of odor in the inlet to the bed was obtained by mixing the main air stream with a second stream of high odor concentration; the latter was contained in a laminated Mylar balloon or a gas cylinder. The desired relative humidity was obtained by humidifying or dehumidifying the main air stream.

***Although it is EPA policy to use metric units in all its reports, certain non-metric units are sed herein for convenience. Readers more familiar with metric units are requested to use the Conversion Factors listed in the Appendix.**

The absorbent filter material was held in position by a stainless steel wire mesh and was compacted gently until a reproducible standard pressure drop across the bed was achieved for a given height of the filter bed. The diameter was usually three inches, although some runs were made with a diameter of one inch. H_2S concentrations in the inlet and outlet streams were determined with a Gelman Model 23000 paper tape sampler utilizing a silver nitrate impregnated tape (Natusch et al, 1972). The optical density of the resulting silver sulfide spot was measured with a Gelman Model 14101 paper tape densitometer. The mercaptans were analyzed by means of a gas chromatograph with a flame photometric detector.

B. Preparation of MnO_2-Sawdust

MnO_2-sawdust was prepared as follows:
After grading for size and drying to ambient moisture content, a 200 gram sample of sawdust was placed in a 1500 ml beaker and soaked in 1000 mls of one percent reagent grade sodium hydroxide solution for two hours. The sodium hydroxide solution was then drained off and the sawdust washed with 1000 mls of water to remove any extracted material.

The sawdust mixture was transferred to a 20 liter Pyrex container, covered with water and heated to 80°C. 200 grams of crushed technical grade granular $KMnO_4$ (Carus Chemical Co.) were then added. The mixture was stirred rapidly and the highly exothermic reaction between sawdust and permanganate was considered complete when it ceased to produce heat. After removal of the liquid, the MnO_2-sawdust was placed on a 20 mesh screen to dry under an exhaust hood. (Note: If this material is taken to complete dryness at a temperature greater than 100°C over a period of days, it can ignite.) The final material has a bulk density of about 0.38 g/cm^3.

No effect of storage life on either the activity or capacity of MnO_2-sawdust for H_2S has been observed over a period of at least two years. The majority of the MnO_2 prepared in this way adheres firmly to the surface of the sawdust (or ground corn cobs) and is not dislodged by passage of air through the sawdust particles.

C. Operating Conditions

Unless otherwise stated, all the filter materials were presented in a one-inch deep and three-inch diameter bed. The particle size was 8 to 10 mesh and air containing the desired concentration of odor at 60% RH and 75°F was passed through this bed at 200 feet per minute. These values were varied individually from the standard conditions given in order to determine the effect of individual parameters on the efficiency and capacity of each filter material.

III. RESULTS

A. HYDROGEN SULFIDE

1. Performance of MnO_2-Sawdust and Activated Carbons

The performance of various adsorbents in removing H_2S from air, under the standard conditions given above, is presented in Figure 1. The ratio of the H_2S concentration in the air leaving the bed (C_o) to the concentration in the inlet stream (C_i) is shown as a function of time.

It is seen that the MnO_2 impregnated fir and hemlock are considerably more efficient in removing H_2S from air than any of the activated carbons tested. (Activated carbons were obtained from Barnebey-Cheney Inc., types CJ, GI, and AC and Pittsburg Activated Carbon, type BPL; type CJ is impregnated with a metal oxide. The bulk density range is 0.41-0.63 g/cm^3). The MnO_2-sawdust filter is at least an order of magnitude better than the carbons over the course of the eight-hour run.

We also investigated the efficiency of ground corn cobs impregnated with MnO_2. As can be seen in Figure 1, this material is less efficient than the MnO_2 -sawdust but more efficient than the activated carbon. The part of the corn cob used in this work is very hard, and the lower efficiency compared to the sawdust substrate may be due to a lower surface area.

In order to run at conditions closer to those which might be obtained in practice, MnO_2-sawdust was tested against three activated carbons at a flow rate of 20 feet per minute and an H_2S concentration of 80 ppm. The results are shown in Figure 2. These results show the performance of the activated carbons relative to MnO_2-sawdust to be somewhat improved with respect to the previous testing conditions. However, none of the activated

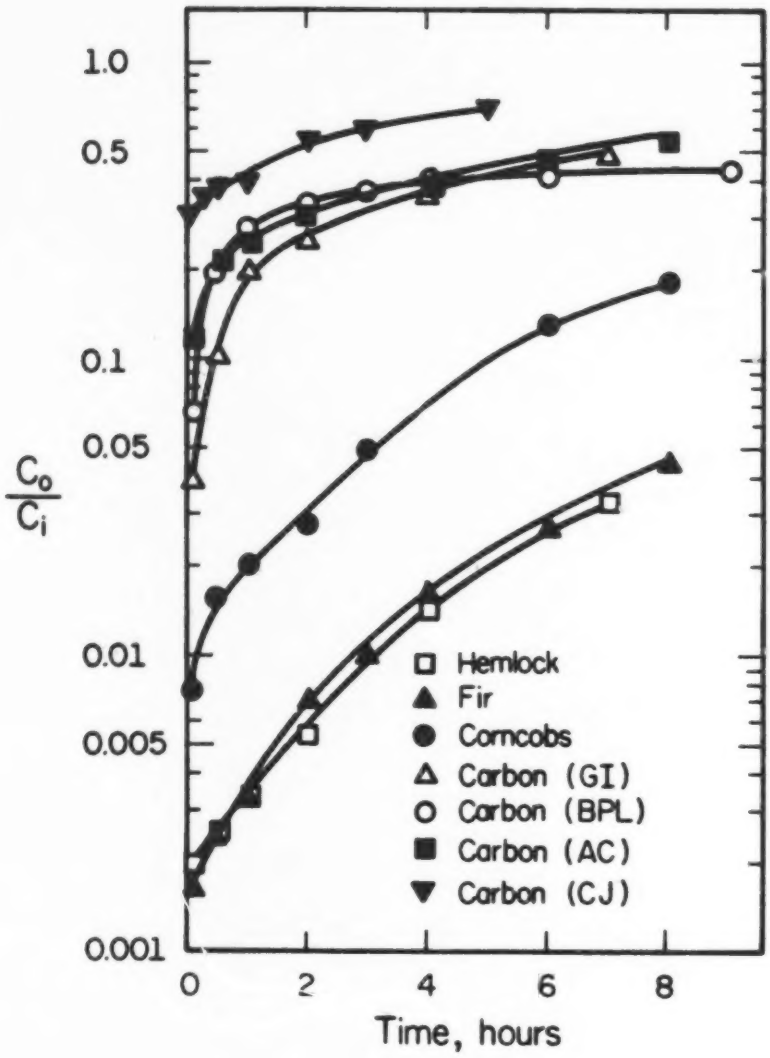


Figure 1. H_2S outlet/inlet concentration ratio vs. time for various materials

200 ft/min, 5 ppm H_2S, 8–10 mesh, 60% relative humidity, 1-in. bed depth, 75°F

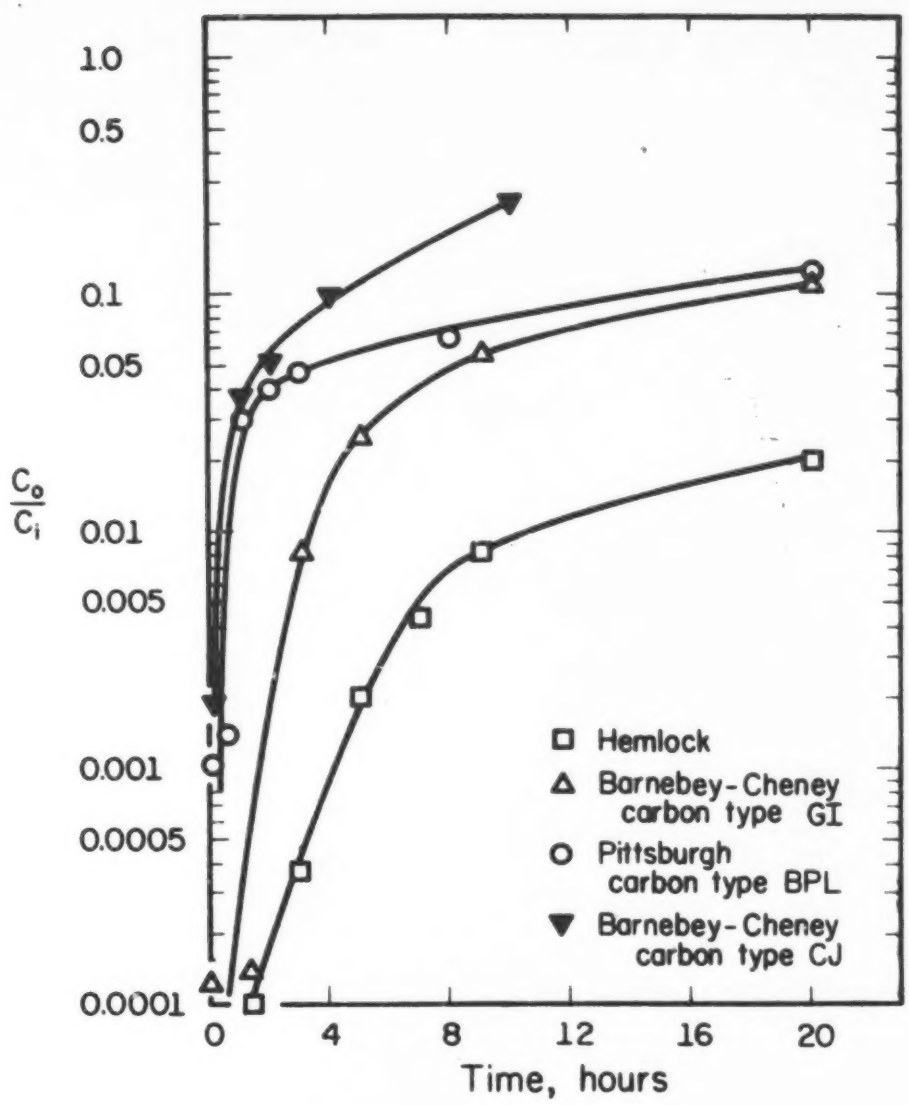


Figure 2. H_2S outlet/inlet concentration ratio vs. time for various materials

20 ft/min, 8–10 mesh, 80 ppm H_2S, 1-in. bed depth, 60% relative humidity, 75°F

carbons is comparable to MnO_2-sawdust in activity.

The foregoing experiments were stopped before the efficiency of H_2S removal had dropped to zero; however, we did carry out a few runs to complete, or nearly complete, bed exhaustion. Some results are shown in Figure 3 (200 ft/min, 5 ppm H_2S) for both MnO_2-hemlock and carbon type GI. At higher concentrations similar results are obtained although both the MnO_2-sawdust and the carbon are exhausted in a shorter time. For example, at 80 ppm and 200 ft/min, the two curves cross at 4-1/2 hours at which time the efficiency of each has dropped to 15%; the hemlock and carbon are exhausted in 8 and 10 hours respectively.

The capacities of these filters can be found by integrating data such as that shown in Figure 3. In this way one obtains the total mass of H_2S which is adsorbed before the filter efficiency drops below some specified value. Capacities in grams of H_2S removed/gram filter are shown in Figure 4 for MnO_2-hemlock and carbon type GI for H_2S inlet concentrations of 5 and 80 ppm as functions of efficiency. The capacities of the MnO_2-sawdust filter are significantly higher than those of the activated carbon. For example, consider an inlet H_2S concentration of 80 ppm. The total H_2S adsorbed by the MnO_2-sawdust before the efficiency drops below 60% is 0.075 g/g whereas for the carbon, it is 0.00425 g/g. For an inlet H_2S concentration of 5 ppm, the sawdust and carbon adsorb 0.084 g/g and 0.0171 g/g, respectively, before the efficiency drops below 60%. The capacity of the hemlock at exhaustion is roughly 0.12 g/g (either H_2S level) while that of the carbon is 0.1 g/g (either H_2S level).

2. Concentrations

The behavior of the MnO_2-sawdust and activated carbon type GI at various H_2S concentrations may be compared as in Figure 5, where the ratio of the H_2S concentrations in the effluent and inlet streams is shown as a function of the total mass of H_2S fed to the filter on a per gram of filter basis. In the case of MnO_2-sawdust, the filter efficiency increases somewhat with the concentration of H_2S passing through the bed.

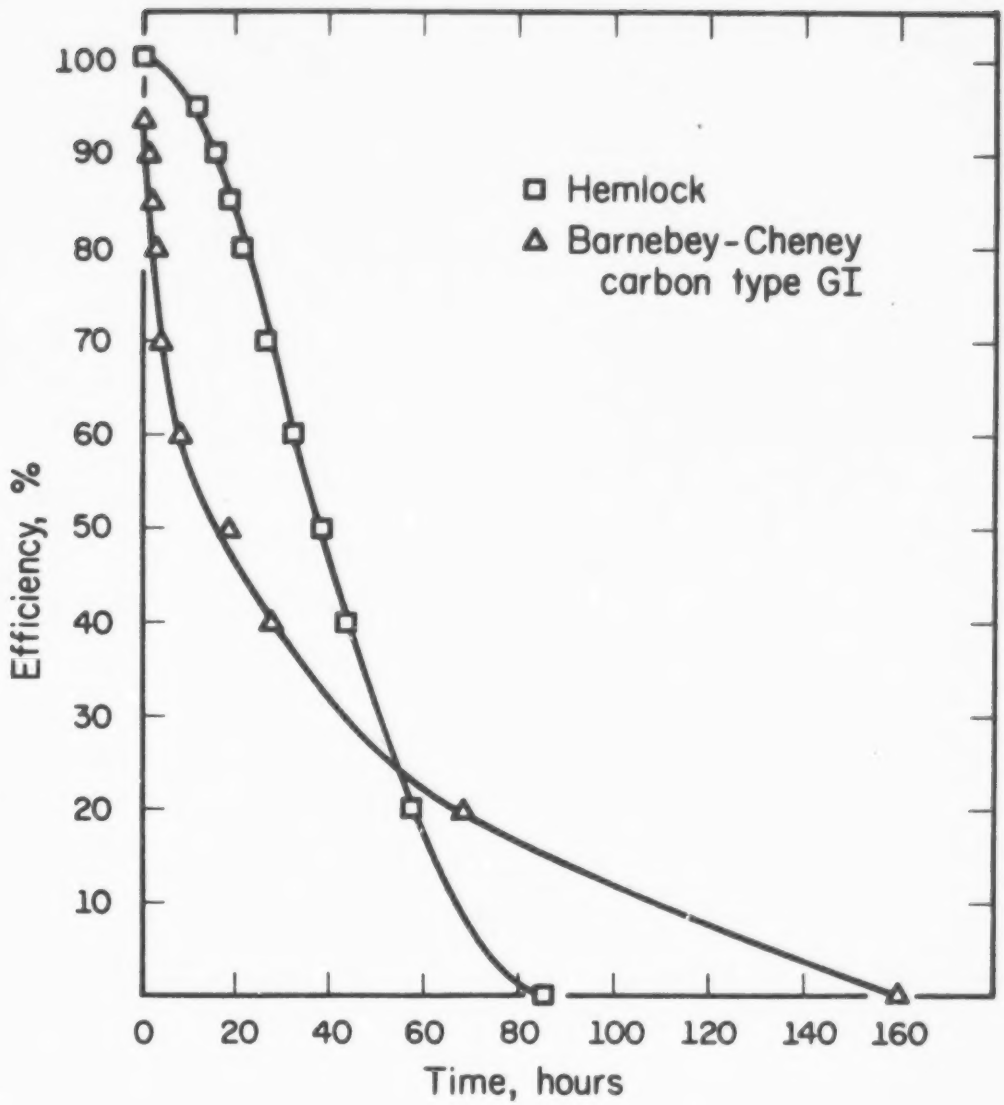


Figure 3. Efficiency vs. time

5 ppm H_2S, 200 ft/min, 8--10 mesh, 1-in. bed depth, 60% relative humidity, 75°F

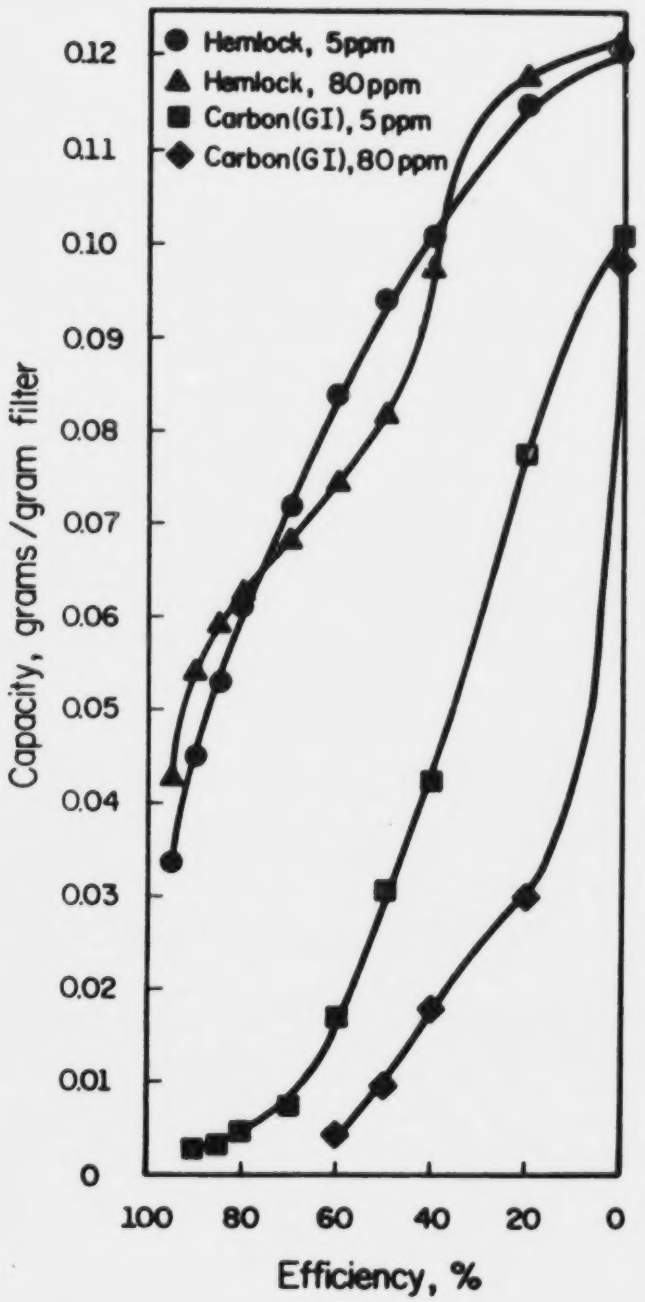


Figure 4. Capacity as a function of desired adsorption efficiency
Bed diameter, 3-in.; bed depth, 1-in.

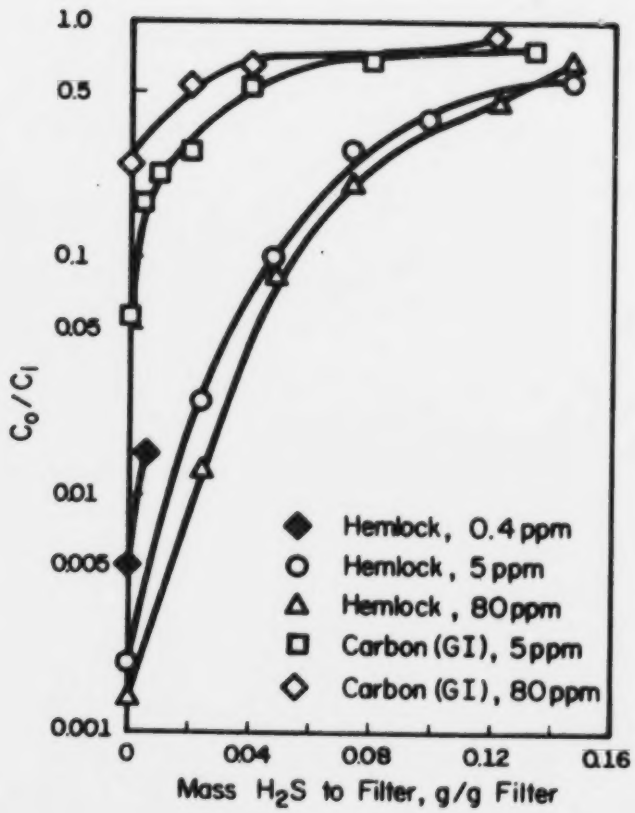


Figure 5. H_2S outlet/inlet concentration ratio vs. mass of H_2S feed

200 ft/min, 1-in. bed depth, 60% relative humidity, 8–10 mesh, 75°F, 3-in. bed diameter

This behavior is consistent with reaction kinetics in which the rate of reaction between MnO_2 and H_2S is a positive function of the H_2S concentration. The activated carbon efficiency, however, varies inversely with H_2S concentration. This is consistent with predictions based on the activated carbon adsorption isotherm (Kipling, 1956).

3. Relative Humidity

The variation of filter activity with relative humidity is shown in Figure 6 for MnO_2-sawdust and carbon type BPL. In Figure 6a the ratio of C_o/C_i at 80% RH to that at any humidity level is shown for both filters $[(C_o/C_i)_{80\% RH}/(C_o/C_i)]$. This ratio is essentially independent of time except at the onset of a run where efficiency is nearly 100% at all humidity levels. The efficiency of MnO_2-sawdust peaks around 80% RH. A similar maximum is often observed for the rate of corrosion of metals by H_2S with varying RH (Backlund, 1966). This maximum is attributed to a reduction in the rate of H_2S reaction at high humidity due to formation of a film of water on the reactive surface. Thus, the rate of mass transfer of H_2S to the surface becomes partially liquid firm controlled. The same effect would also be expected to occur for activated carbon; however, it should be much less apparent due to the lower activity of the carbon. In practice no convincing activity peak is observed for activated carbon.

In Figure 6b is shown the variation of C_o/C_i with time at RH = 80%. MnO_2-sawdust is superior in performance to the activated carbon at all RH levels; however, neither performs well at low humidities (<20% RH). Figure 6 provides a concise design basis for efficiency variation with time at all RH levels. For hemlock:

$$\log [(C_o/C_i)_{80\% RH}/(C_o/C_i)] = 3.19 \log (RH) - 6.06 \quad 20\% \leq RH \leq 80\%$$
$$= -13.6 \log (RH) + 25.9 \quad 80\% \leq RH \leq 90\%$$

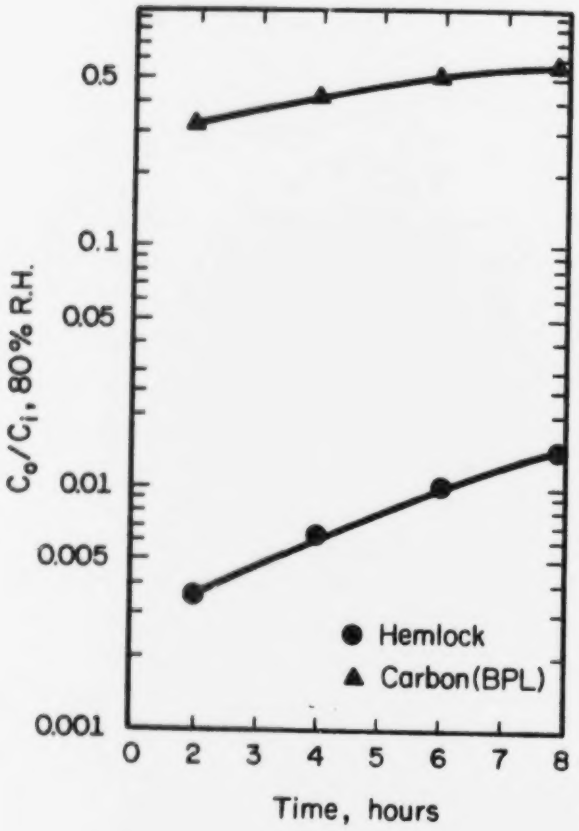


Figure 6a Dependence of H_2S outlet/inlet concentration on relative humidity

5 ppm H_2S, 200 ft/min, 1-in bed depth, 75°F, 8-10 mesh

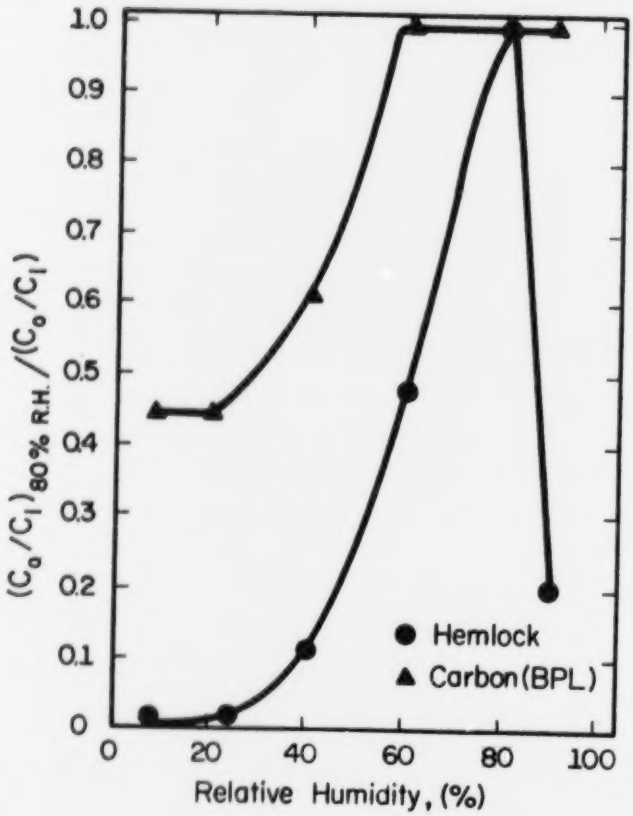


Figure 6b Dependence of H_2S outlet/inlet concentration on time for RH=80%.
(Conditions as in 6a)

4. Temperature

Preliminary studies were conducted to determine whether the activity and capacity of MnO_2-sawdust depend on temperature at constant relative humidity (40% RH). No substantial effect was observed over the temperature range 75-113°F. In this narrow temperature range any increase in the rate of chemical reaction may be offset by a decrease in the rate of adsorption of reactant. Control by diffusion or mass transfer would also explain the experimental temperature behavior. The latter is suggested by results presented in this paper.

5. Residence Time

The activity dependence of MnO_2-sawdust on the flow rate of air passing through the filter bed is shown in Figure 7. No capacity data are available for Figure 7, although filter capacity is expected to be essentially independent of flow rate unless autoregenerative processes take place.

The dependence of the activity of MnO_2-sawdust on the depth of the filter bed was also investigated. The ratio of the concentration of H_2S in the outlet stream to that of the inlet, of course, decreases as the depth of the bed is increased. If there were no mass transfer or channeling effects and if the activity were independent of H_2S concentration, the ratio should initially decrease exponentially with increasing bed height; if the ratio decreases by some multiplicative factor when the bed depth is increased from one to two inches, it should decrease by the same factors when the bed depth is further increased to three inches. In practice, the change from two to three inches is somewhat less. For example, at the conditions of Figure 1, the ratio C_o/C_i at the beginning of a run is 0.002, 0.0006, and 0.0004 for bed depths of one, two, and three inches, respectively.

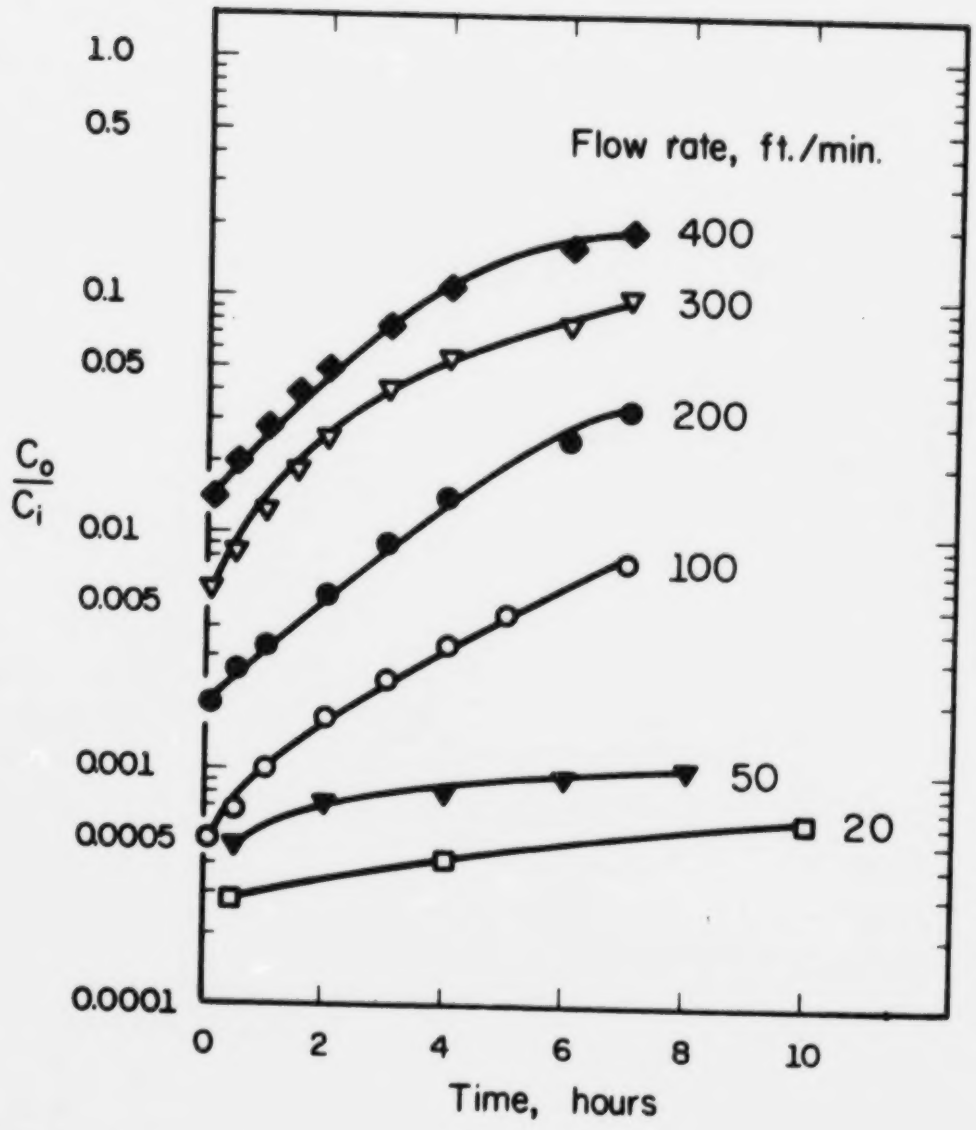


Figure 7. H_2S outlet/inlet concentration ratio vs. time for varying flow rates

5 ppm H_2S, 8–10 mesh, 1-in. bed depth, 60% relative humidity, hemlock, 75°F

6. Mass Transfer Effects

An H_2S molecule in the gas stream must be transported to the surface of the solid MnO_2-sawdust before it can react. A high free gas stream velocity reduces the external mass transfer resistance. Thus, by varying the gas flow rate and the filter bed depth simultaneously so as to maintain a constant residence time, the importance of mass transfer limitations in the filter bed can be assessed. The results of such an experiment are shown for MnO_2-sawdust in Figure 8.

Clearly under these experimental conditions there is a significant mass transfer reduction in the efficiency of adsorption of H_2S-sawdust.

7. Particle Size

The dependence of H_2S removal on particle size for MnO_2-hemlock and carbon type BPL is given by:

$$R = 5.48 \times 10^{-7} d_p^{-2.87} \qquad MnO_2\text{-hemlock}$$

$$= 2.48 \times 10^{-3} d_p^{-1.19} \qquad \text{Carbon (BPL)}$$

R is the ratio of the quantity (C_o/C_i) for mesh size 8-10 Tyler to that at any given mesh size. $[R = (C_o/C_i)_{8\text{-}10\ mesh}/(C_o/C_i)]$. This value is independent of time except initially where conversion is approximately 100% for all mesh sizes. The characteristic material dimension, d_p, in feet, was taken as the average aperture opening for a given mesh size range. The above correlations were determined at a superficial gas velocity of 200 ft/min, H_2S concentration of 5 ppm, 60% RH, 75°F, and one inch bed depth for a mesh size range 4-14 Tyler. These correlations may be used in conjunction with Figure 1 for rough design purposes. As expected, the rate of H_2S removal increases monotonically as the particle size is decreased from 4-6 to 10-14 mesh. It should be noted that even the largest sawdust tested (4-6 mesh) is a more efficient adsorbent than the smallest carbon (10-14 mesh). For both the MnO_2-sawdust and the carbon, the H_2S removal efficiency increases with decreasing particle size because of the reduction of mass transfer resistance within the particles. For the MnO_2-sawdust adsorbents, there is also the additional factor that the smaller

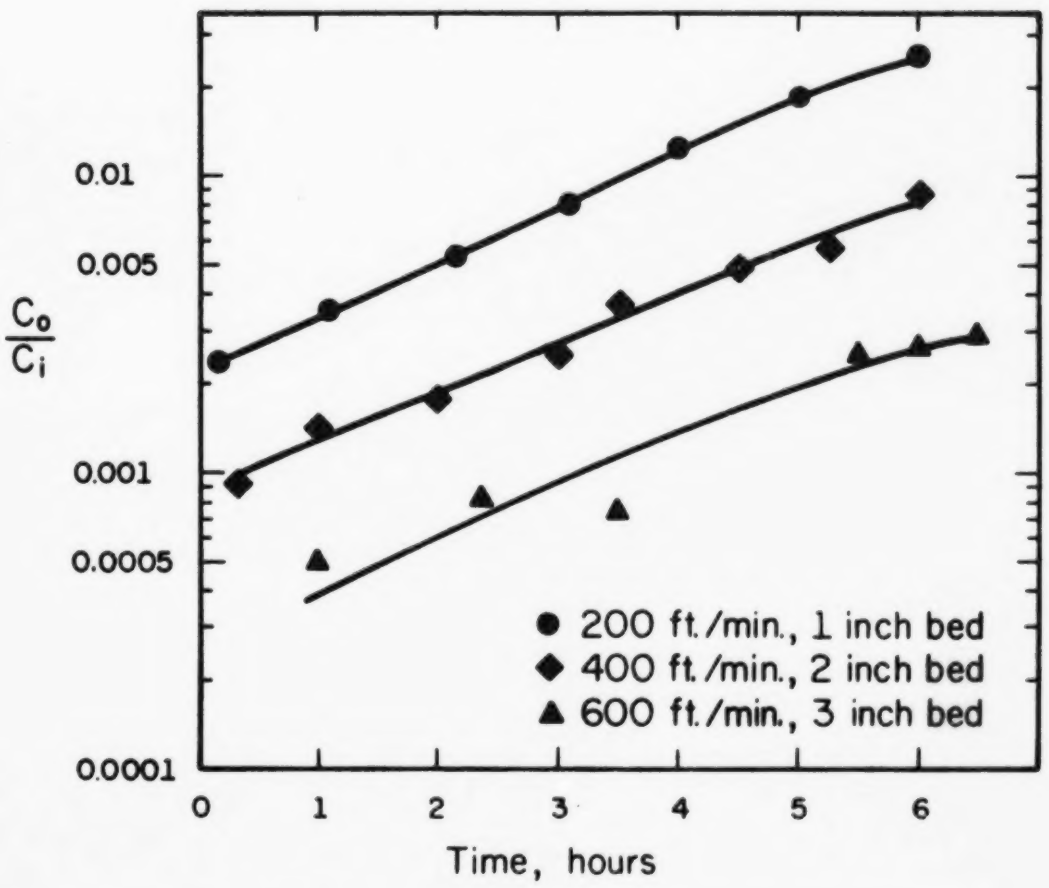


Figure 8. H_2S outlet/inlet concentration ratio for constant residence times and varying flow rates
8–10 mesh, 5 ppm H_2S, 60% relative humidity, 75°F

particles probably contain a larger mass of MnO_2 per unit bed volume since the MnO_2 is found only in a layer near the outside of the sawdust particles.

8. Pressure Drop

We have measured the pressure drop across the bed of MnO_2-sawdust at velocities up to 300 ft/min for various mesh sizes. The pressure drop $\Delta p/L$ (inches H_2O/ft bed) is given by

$$\frac{\Delta p}{L} = av^{1.26}$$

a = .017	4-6 mesh Tyler
= .044	8-10 mesh Tyler
= .054	10-14 mesh Tyler

where v is the superficial gas velocity in ft/min. The pressure drops are similar to those across a bed of carbon (Adsorption Handbook, 1973).

9. Optimization

No attempt was made in this work to optimize the performance of MnO_2-sawdust by varying preparative parameters. Preliminary investigations have, however, indicated that considerable improvement in the performance of MnO_2-sawdust can be achieved by varying a number of preparational parameters. These studies will be reported later.

10. Summary

The foregoing performance tests have clearly established the superiority of MnO_2-sawdust over some of the better activated carbons for the absorption of H_2S. However, while MnO_2-sawdust can be readily prepared, it is not commercially available at present and must be discarded after use. In practice, activated carbon used in odor control applications is rarely regenerated. The possibility of regeneration is attractive and is being investigated for MnO_2-sawdust.

MnO_2-sawdust has the disadvantage that it will ignite if allowed to dry out completely over a period of days at a temperature above 100°C.

The material has remained stable when operated for a period of weeks at temperatures over 100°C in the presence of steam and even when ambient air (70°F, 55% RH) is heated to 120°C and passed through the bed. However, high temperature (>100°C) operation should be approached with caution. The problem can be overcome by presenting the active MnO_2 on non-flammable substrates such as pumice, vermiculite, perlite or coke although there is a marked decrease in performance (Natusch and Sewell, 1970).

In attempting to make a general correlation for the behavior of the MnO_2-sawdust in fixed bed applications for H_2S removal, one realizes that the system is transient, that there are substantial mass transfer effects both within and outside the particles and that the reaction kinetics are unknown. The task is thus quite difficult and only part of the picture is available. It is already clear that many physical and chemical properties of the MnO_2 present on MnO_2-sawdust are quite different from those of any other MnO_2 yet reported (Bienstock and Field, 1960; Korshunov and Vereshchagin, 1966). The material appears to be most similar to δ-MnO_2.

The overall reaction of MnO_2-sawdust with H_2S can be written

$$MnO_2 + 2H_2S \rightarrow MnS + S + 2H_2O$$

indicating that one mole of MnO_2 is capable of adsorbing two moles of H_2S. For the MnO_2-sawdust utilized herein a standard one-inch deep bed (diameter = 3 inches) contains 40 g of MnO_2-sawdust which in turn contains approximately 11.8 g of MnO_2. For this bed configuration calculations based on the results given in Figure 3 show that only about half the total MnO_2 reacts with H_2S before the bed is exhausted. Additional capacity can, however, be obtained by agitating the exhausted MnO_2-sawdust so as to expose fresh MnO_2.

Work is presently in progress on the basic nature of the MnO_2-sawdust in order to produce a more active filter material and on obtaining and correlating further data necessary for design of filter beds under a variety of conditions.

B. MERCAPTANS

N - butanethiol and methanethiol were investigated. Air containing one to fifty ppm thiol was passed through the MnO_2-sawdust for several hours. Inlet and outlet gas analyses were made with a Tracor Model 550 chromatograph with a flame photometric detector. As with H_2S, all runs were made at or near room temperatures. In contrast to the situation with H_2S, however, the filter did not simply adsorb the mercaptan, but acted catalytically to convert the n - butanethiol to a disulfide. The efficiency of n - butanethiol removal was 90% to 99.9% depending on contact time. All this mercaptan was converted to the disulfide and no decrease in efficiency of the filter was noted with time. Since the MnO_2-sawdust is acting catalytically rather than as an absorbent, the filter in its present form is inferior to activated carbon in removing mercaptan from air. However, no attempt has yet been made to optimize the filter material for mercaptan control and it is possible that further studies could find a MnO_2-sawdust preparation useful for mercaptans. In its present form, the MnO_2-filter could be used along with activated carbon for simultaneous removal of H_2S and mercaptans.

When dry nitrogen was used in place of air to carry the mercaptans, the filter acted as an adsorbent rather than catalytically and the efficiency of the filter decreased with time.

C. AMINES

Preliminary studies were made on normal hexyl amine. The results, to date, show that although some amine is removed, the MnO_2-sawdust filter presently being used is inferior to carbon BPL. For example, at a concentration of 3.5 ppm, a flow rate of 50 ft/min, a bed height of 6 inches, a relative humidity of 60% and a temperature of 76°F, both MnO_2-sawdust and carbon BPL initially remove greater than 95% of the amine. However, the efficiency of the MnO_2-sawdust decreased to zero over a period of five hours whereas that of the carbon remains essentially constant.

IV. FUNDAMENTAL STUDIES ON MnO_2-SAWDUST

A large batch of MnO_2-sawdust (Preparation 20) was prepared in the standard method described previously. Large quantities of MnO_2 shaken off of the impregnated sawdust (20-A), MnO_2 decanted from the reaction solution (20-B), and MnO_2 formed by reaction between the 1% NaOH extract of the sawdust and potassium permanganate (20-C) were also obtained.

An extensive series of tests for these materials was carried out. When methods of preparation other than the standard method are used, the same series of tests was carried out on the products. It was then possible to correlate the activity of the MnO_2 and MnO_2-sawdust with several of the fundamental properties and this will serve as a guide for optimization of filter performance.

A. Standard Preparational Procedure

1. Materials

(I) Wood 200g sawdust

(II) NaOH Solution 10g NaOH in 1 liter de-ionized water

(III) $KMnO_4$ 200g Carus Chemical Co.

2. Procedure

(I) soaked in (II) for two hours. Soaking solution decanted and saved. Sawdust washed once with 1 liter de-ionized water. Sawdust covered with de-ionized water and heated to 80°C. Crushed III added and solution stirred to the end of the reaction. All material flushed down the sides of the reaction vessel into bulk solution. Mixture is allowed to set 15 minutes. The liquid is decanted and saved. The impregnated sawdust is air-dried for two days. After drying, the material is shaken loosely on a screen (20 mesh). Material shaken off is sieved > 100 mesh (Tyler) and is labelled A sample (MnO_2 shake-off). The decanted liquid is vacuum filtered and washed 3x. The filtered solid is air dried and labelled B sample (MnO_2 decant). The filtered extract solution is reacted with 20g $KMnO_4$ at 80°C and filtered. The resultant powder is called C sample (extract).

B. Hemlock, $KMnO_4$, NaOH Preparation

In previous work, MnO_2 impregnated sawdust preparations prepared from hemlock were found to give the greatest activity. Therefore, the first material prepared was a batch using 8 x 10 mesh (Tyler) hemlock. The relative activities toward H_2S of the activated MnO_2-sawdust (Preparation 20), the shakeoff MnO_2 powder (Preparation 20-A), decanted MnO_2 powder (Preparation 20-B), and the extract MnO_2 powder (Preparation 20-C) are shown in Figure 9. In order to obtain measureable activities for 20A and 20B, it was necessary to dilute the MnO_2 powders with inert glass (170-230 mesh). A weight ratio glass; powder of 3.5:1.0 was used in all experiments. The high pressure drops across the reactor bed did not allow the high gas velocities possible with the sawdust. Complete data for Figure 9 are given in Table I.*

In general, the MnO_2-wood samples were run at about 5 ppm H_2S while the powder/glass samples were run at about 100 ppm H_2S. The activity of the powders was always in the order decant > shakeoff > extract.

In examining the various MnO_2-sawdust and MnO_2 powder preparations a series of chemical and physical properties was determined. The most important of these and the method of determination were:

(1) BET Surface Area -- Orr Surface Area Analyzer
(2) Conc. K^+ -- Atomic Emission Spectroscopy
(3) Conc. Na^+ -- Atomic Emission Spectroscopy
(4) %C -- CO_2 Evolution
(5) %Mn -- EDTA Analysis
(6) Mn Valence State -- Active Oxygen Method

The data are tabulated in Table II.* Differences between the 20A, 20B, and 20C powders may be attributed to surface area differences. Large amounts of potassium are incorporated into the sawdust and powders. The relative amount of Mn in the (IV) oxidation state is a significant indicator of the activity. If the total Mn is determined independently by EDTA titration and if the assumption is made that

*Tables I and II are in the Appendix.

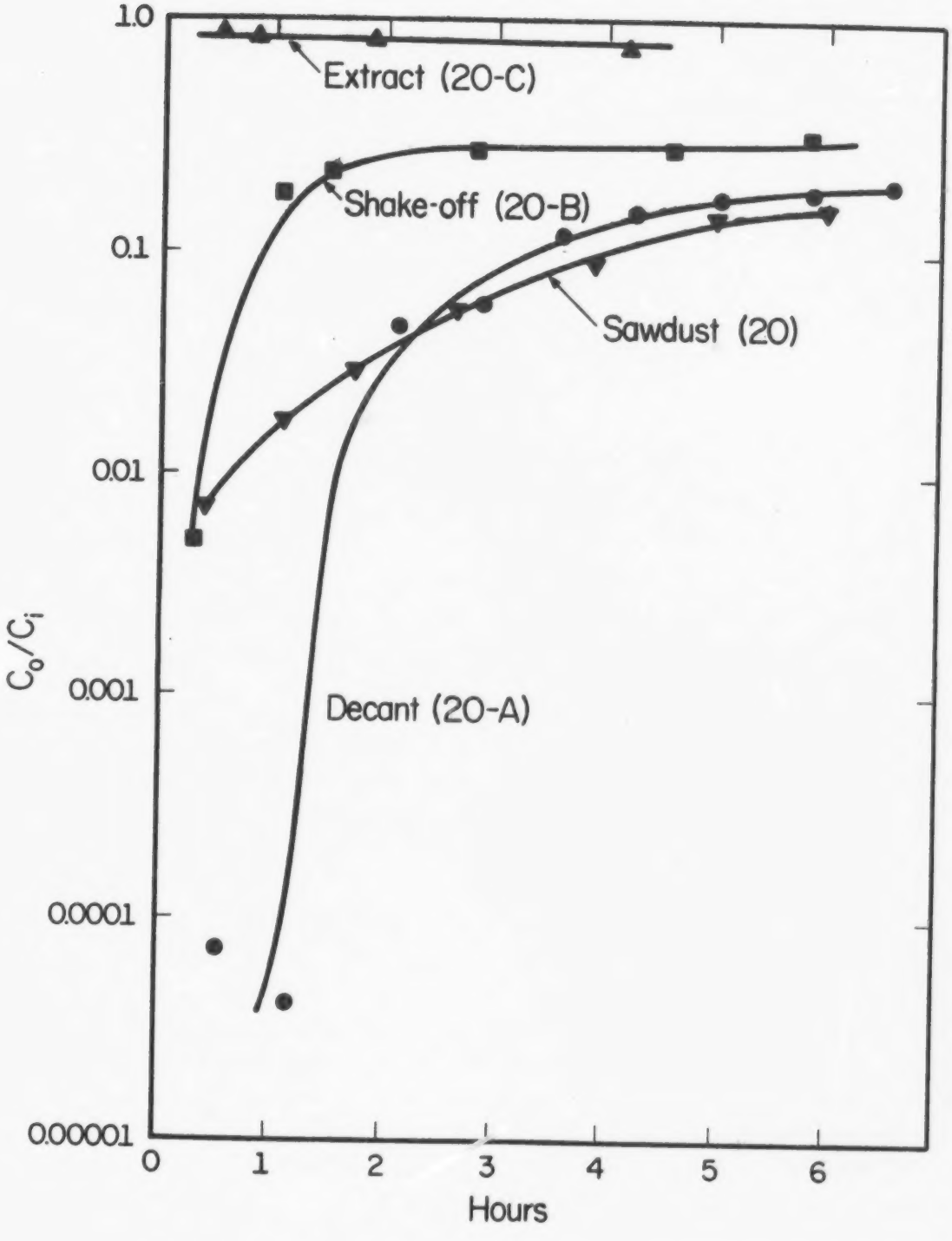
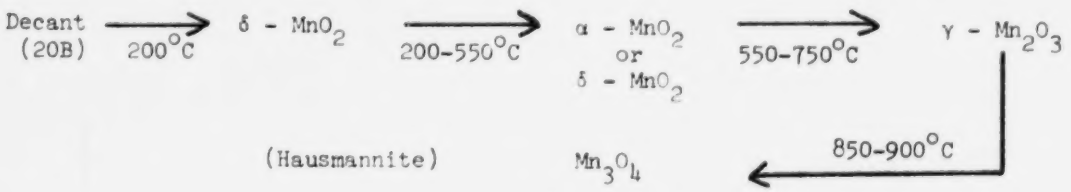


Figure 9 H_2S outlet/inlet concentration vs. time for various Hemlock, $KMnO_4$, NaOH preparations.

no Mn(II) is present, then the relative amounts of Mn(IV) and Mn(III) can be determined by reduction of the "MnO_2" in acidic iodide solution and titration of I_2 formed by standard thiosulfate solution. The ratio of Mn(IV)/Mn(III) is usually about 3:1. The shakeoff samples are not homogeneous and thus a range of composition is indicated for these samples in Table II.

We note that the shakeoff, although more closely related to the impregnated sawdust, is substantially less active than the decanted manganese dioxide. If one could characterize the decant and how it differs from the shakeoff, it may be possible to improve the sawdust. X-ray diffraction patterns at room temperature of both shakeoff and decant indicate no lines or a few unidentifiable lines. Differential thermal analysis when coupled with X-ray diffraction of the heated products has given some interesting data from which the following thermal transformation scheme may be deduced:



The initial heating drives off water and causes a slight ordering of the crystal structure. Hence 20B (decant) is most closely related to δ - MnO_2. The shakeoff material has not yet been characterized by the DTA-x-ray diffraction combination.

C. Hemlock, $NaMnO_4$, NaOH Preparation

In order to determine if the cation in the permanganate affects the sawdust activity, $NaMnO_4$ was substituted for $KMnO_4$ in the preparation procedure. The ionic radii of K^+ and Na^+ are 1.33A° and 0.97A° respectively. Results are shown in Figures 10, 11 for 8 x 10 mesh Hemlock wood. Run conditions for the 21 series materials are similar to the series 20 runs in Figure 9 (see Table I) except in Figure 11 the superficial velocity for all materials was 35 ft/min.

The activity of the MnO_2-sawdust prepared from $NaMnO_4$ is much lower than that prepared from $KMnO_4$. The activity of the shakeoff from the $NaMnO_4$

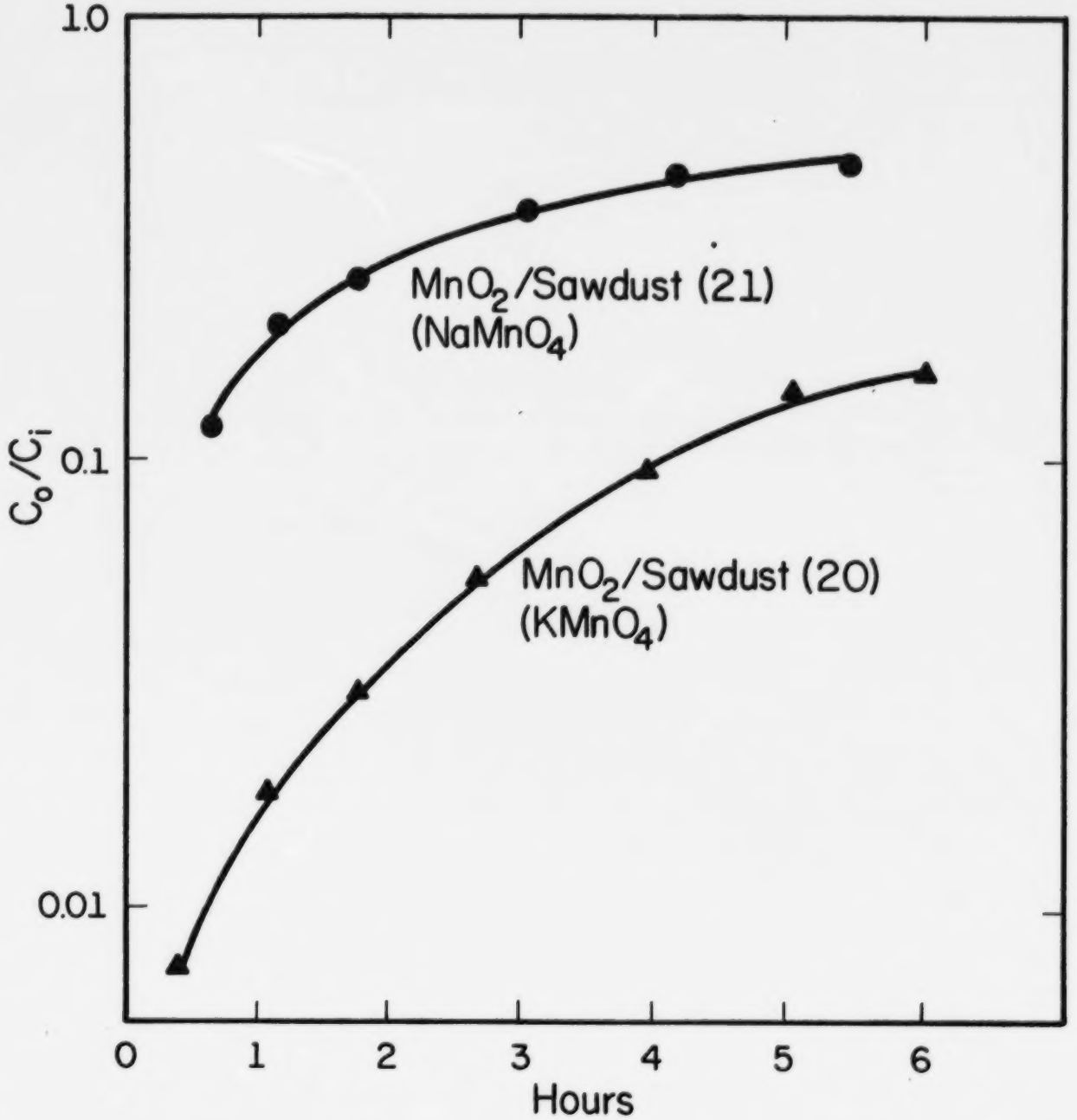


Figure 10 Effect of substituting $NaMnO_4$ for $KMnO_4$ in standard preparation - activity vs. time for sawdust

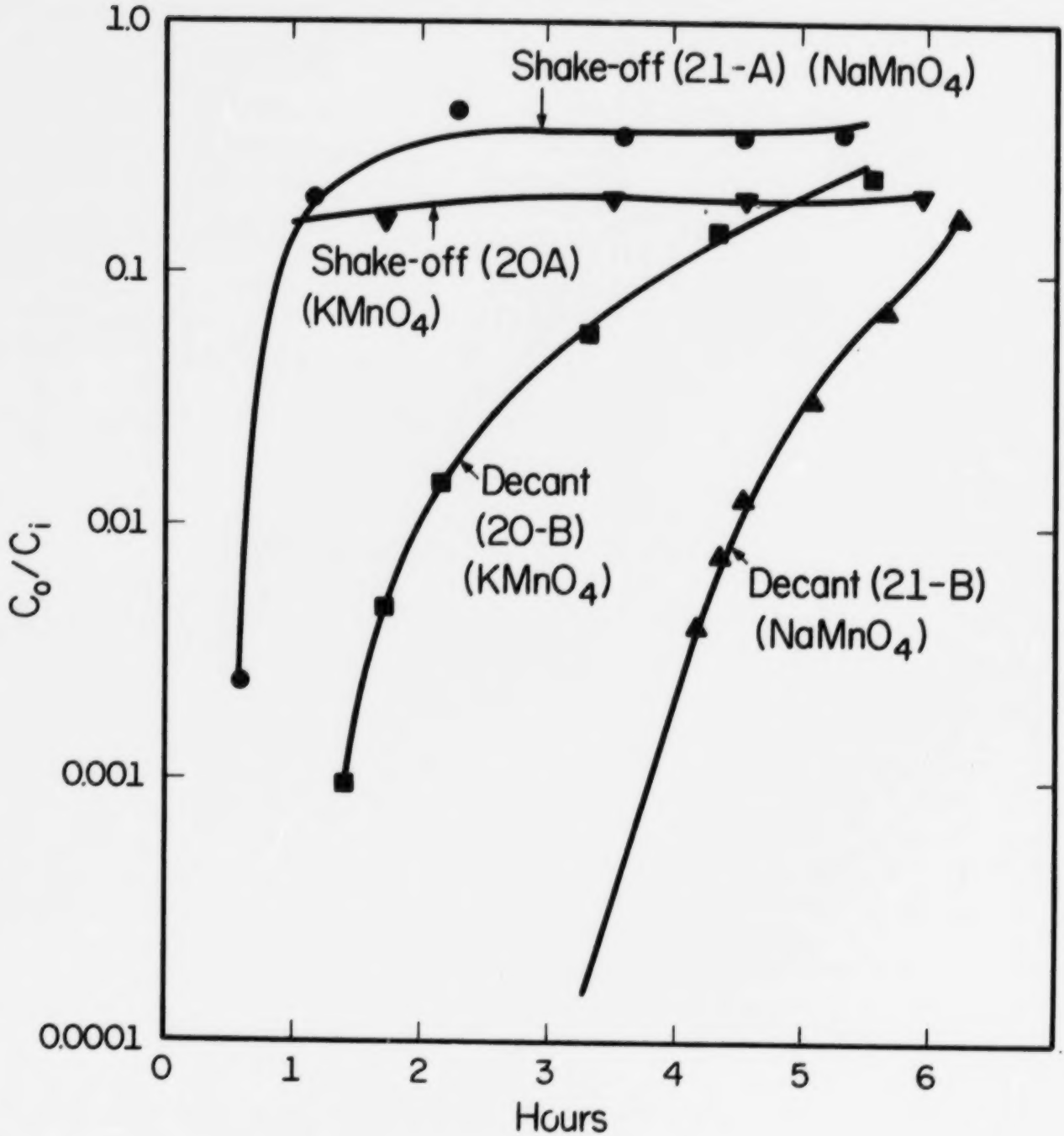


Figure 11 Effect of substituting $NaMnO_4$ for $KMnO_4$ in standard preparation - activity vs. time for powders

preparation is also lower than the shakeoff from the $KMnO_4$ preparation. However, the decanted MnO_2 prepared from $NaMnO_4$ has a higher activity than that from potassium permanganate.

Comparison of the properties of the sawdust prepared form $KMnO_4$ with those of the sawdust prepared from $NaMnO_4$ indicates that the higher activity of the former may be due to its much higher concentration of K^+. The same holds for the shakeoff material. However, by this rationale the decant from $KMnO_4$-(20-B) would be more active than the corresponding 21-B. This is not true. We hypothesize that K^+ stabilizes the active form of MnO_2 during formation at the sawdust-solution interface in such a way that more of the MnO_2 remains physically attached to the sawdust. Because the Na^+ ion is smaller, it does not so stabilize the active MnO_2 "lattice". Some data support this hypothesis (less MnO_2 sawdust formed from $NaMnO_4$ + sawdust, lower surface area) but some do not (same % Mn in the product, approximately the same Mn(IV)/Mn(III) ratio). The MnO_2 powder not adhering to the sawdust in the $NaMnO_4$-sawdust reaction (decanted MnO_2) is presumably more active because, in the absence of K^+ ion, a more amorphorus though less adhesive MnO_2 sample is formed.

D. Hemlock, $KMnO_4$, KOH Preparation

Since high concentrations of K^+ may increase the sawdust activity, a standard preparation of 8x10 mesh Hemlock was made using a 1% KOH soaking solution instead of a NaOH solution. The results are shown in Figures 12 and 13. Run conditions for the 24 series materials are the same as for the series 20 and 21 materials in Figures 10 and 11. The new sawdust preparation is inferior to the standard preparation using NaOH. The decanted and shakeoff material prepared for KOH have about the same activity as the corresponding powders prepared from NaOH.

Properties of these materials are shown in Table II. Substitution of KOH for NaOH did not lead to appreciably higher K^+ levels in the material. The decrease in activity of the MnO_2 sawdust may be due to reduction of the ratio of Mn(IV)/Mn(III); this ratio is about 1:1 in preparation 24 (from KOH) compared to about 3:1 in the standard NaOH preparation. Mn(IV) oxide is the more active form so formation of relatively more Mn(III) would reduce the

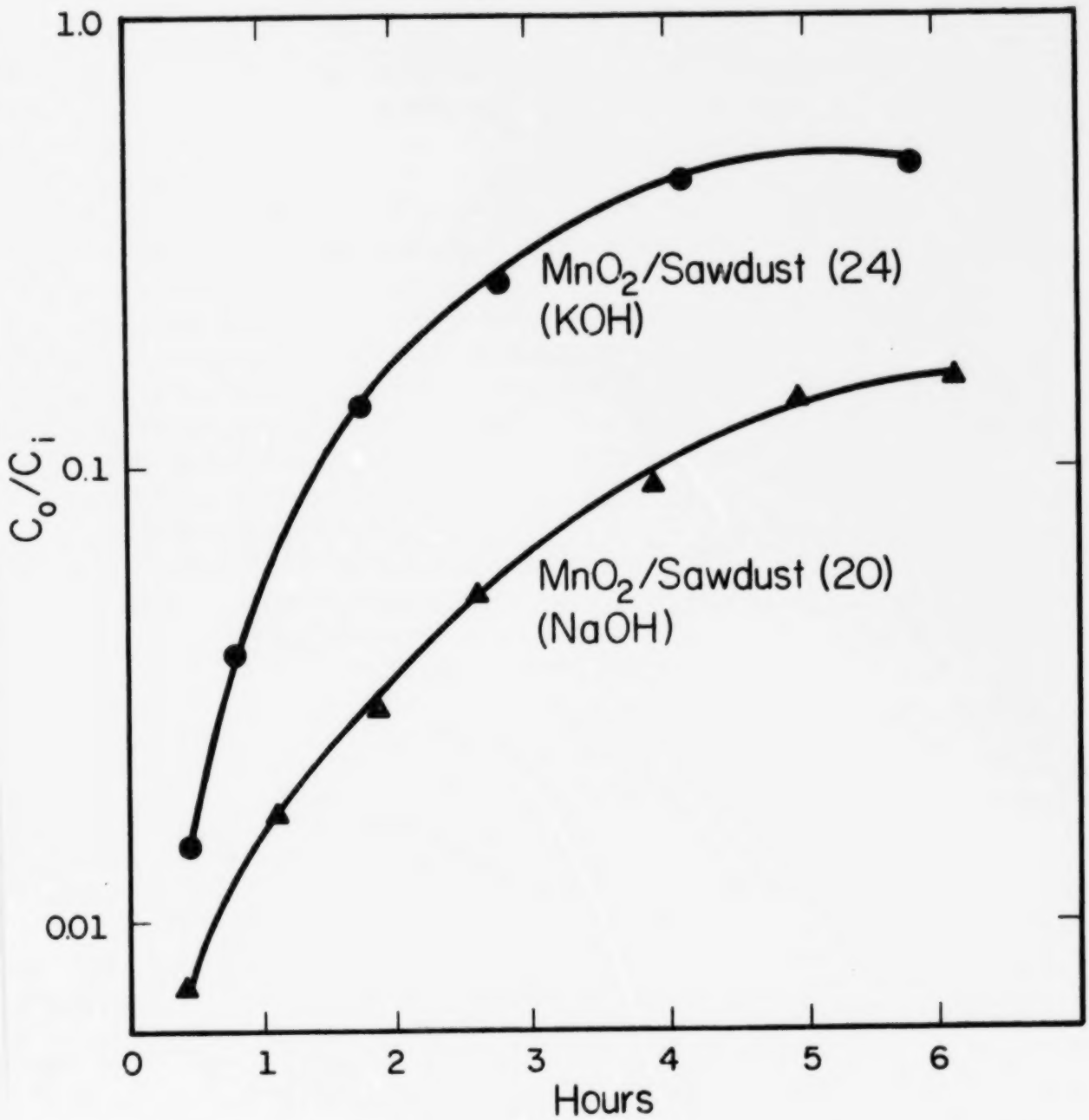


Figure 12 Effect of substituting KOH for NaOH in standard preparation - activity vs. time for sawdust

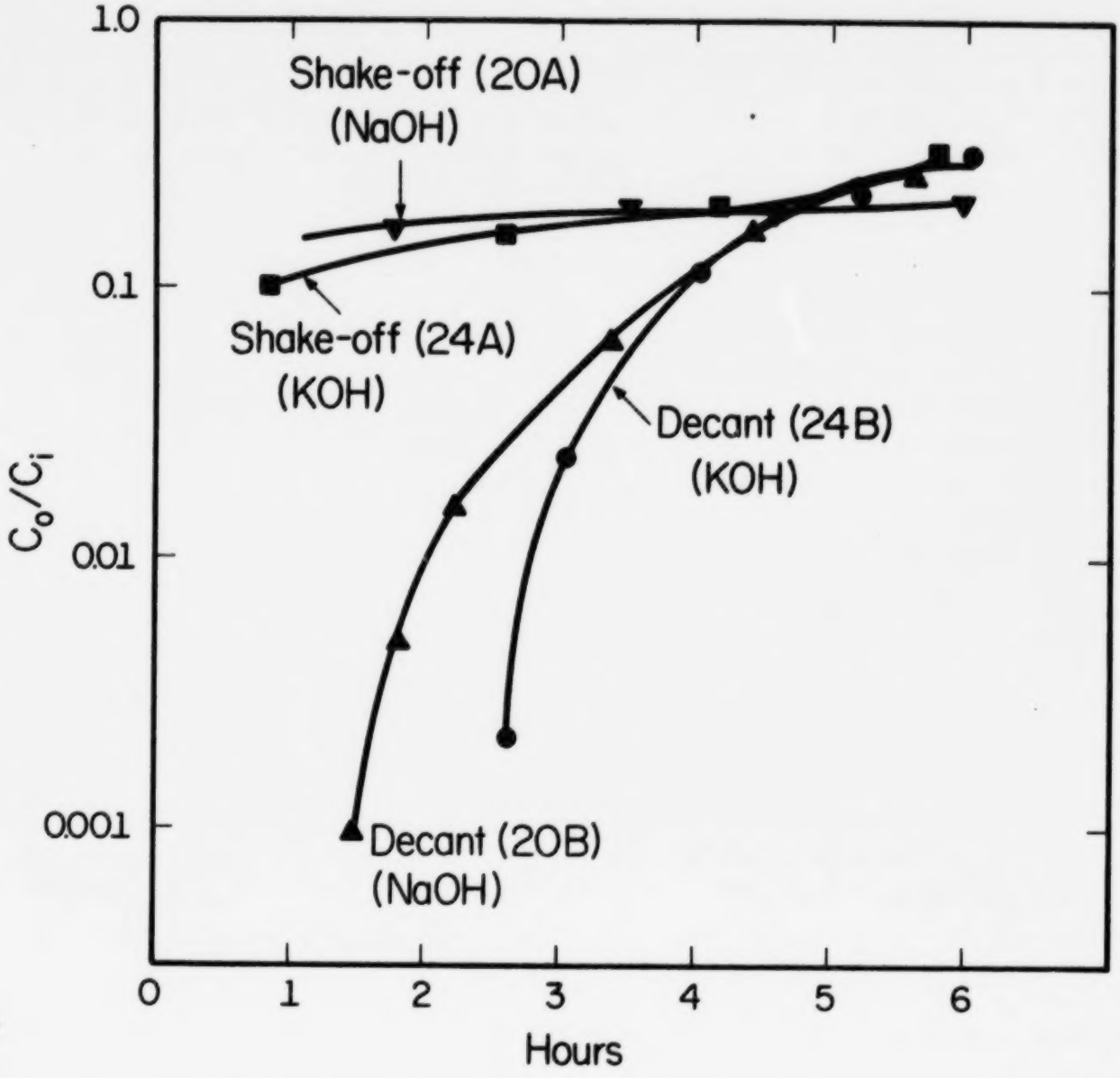


Figure 13 Effect of substituting KOH for NaOH in standard preparation - activity vs. time for powders

MnO_2-sawdust activity. Since the MnO_2 powders (shakeoff and decant) do not show this reduced Mn(IV)/Mn(IV) ratio, it is probable that KOH-treated sawdust exhibits greater reducing properties toward permanganate than does NaOH-treated sawdust. Thus, the cation used for base treatment is significant and this treatment may affect the reducing properties of the sawdust as well as expanding it physical structure.

E. Method of Addition of $KMnO_4$

The manner of addition of the permanganate to the wood is not an important experimental parameter. The standard preparation was modified in that the $KMnO_4$ was added to the sawdust as an aqueous solution at 80°C. For these experiments 8x10 mesh pine was used. Results are shown in Figure 14. Run conditions same as for Preparation 20 in Table I. In addition, it is seen that the pine is inferior to the hemlock. Several of the properties of the pine/MnO_2 are shown below.

Preparation	Run No	Prep. No.	Surface Area m^2/g	%C wt	%Mn wt
8 x 10 Pine Std. Prep.	719	22	4.87	25.96	16.09
8 x 10 Pine Std. Prep. but $KMnO_4$ addition in solution	720	23	6.73	27.34	17.64

F. Reproduction of Catalyst

To determine the reproducibility of catalyst manufacture several batches of 6x8 mesh Hemlock were used to make activated sawdust by the standard method. Results shown in Figure 15 indicate little difference between the preparations. Run conditions were as in Table I for Preparation 20.

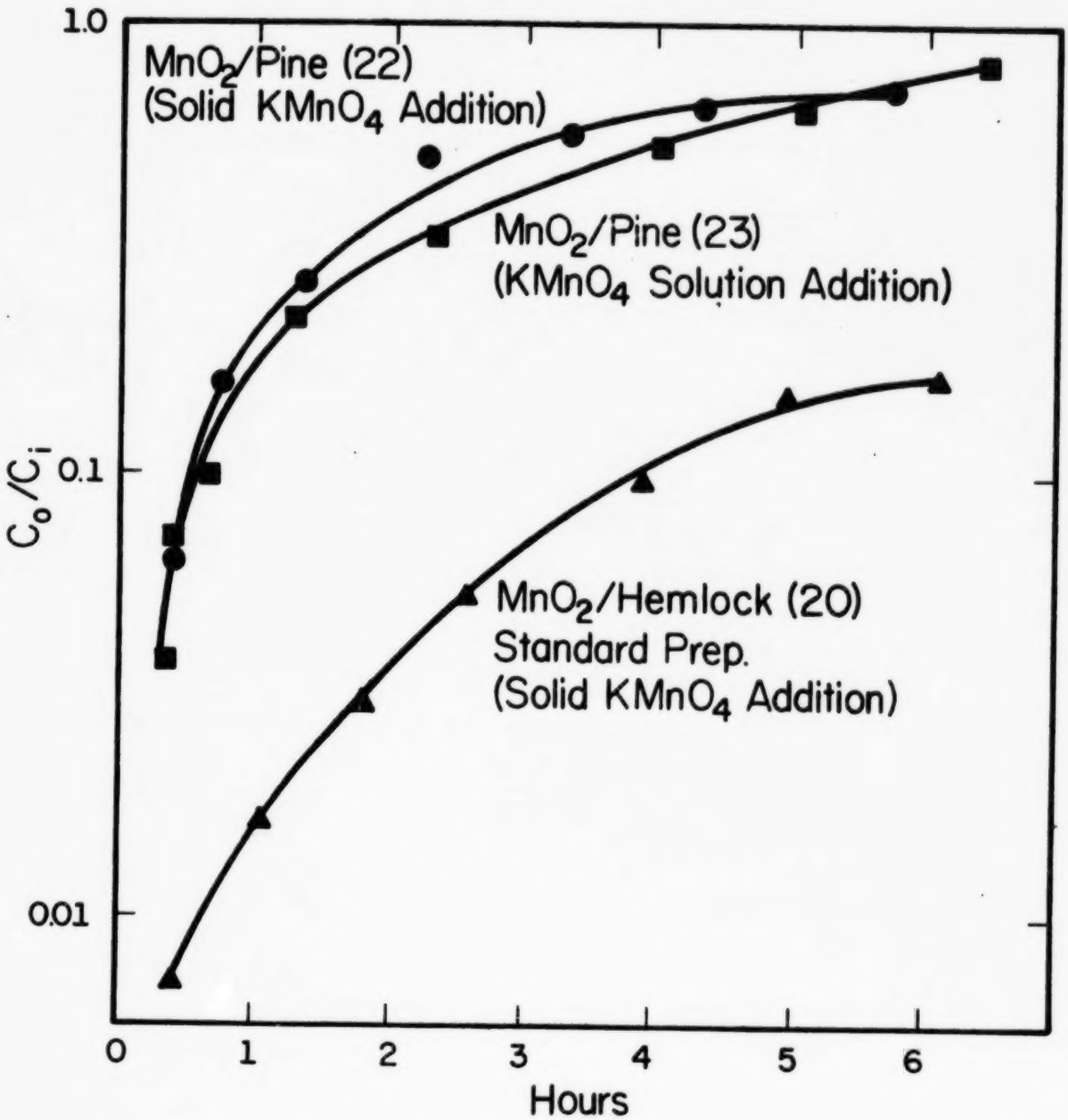


Figure 14 Effect of method of addition of $KMnO_4$ on standard preparation - activity vs. time for sawdust

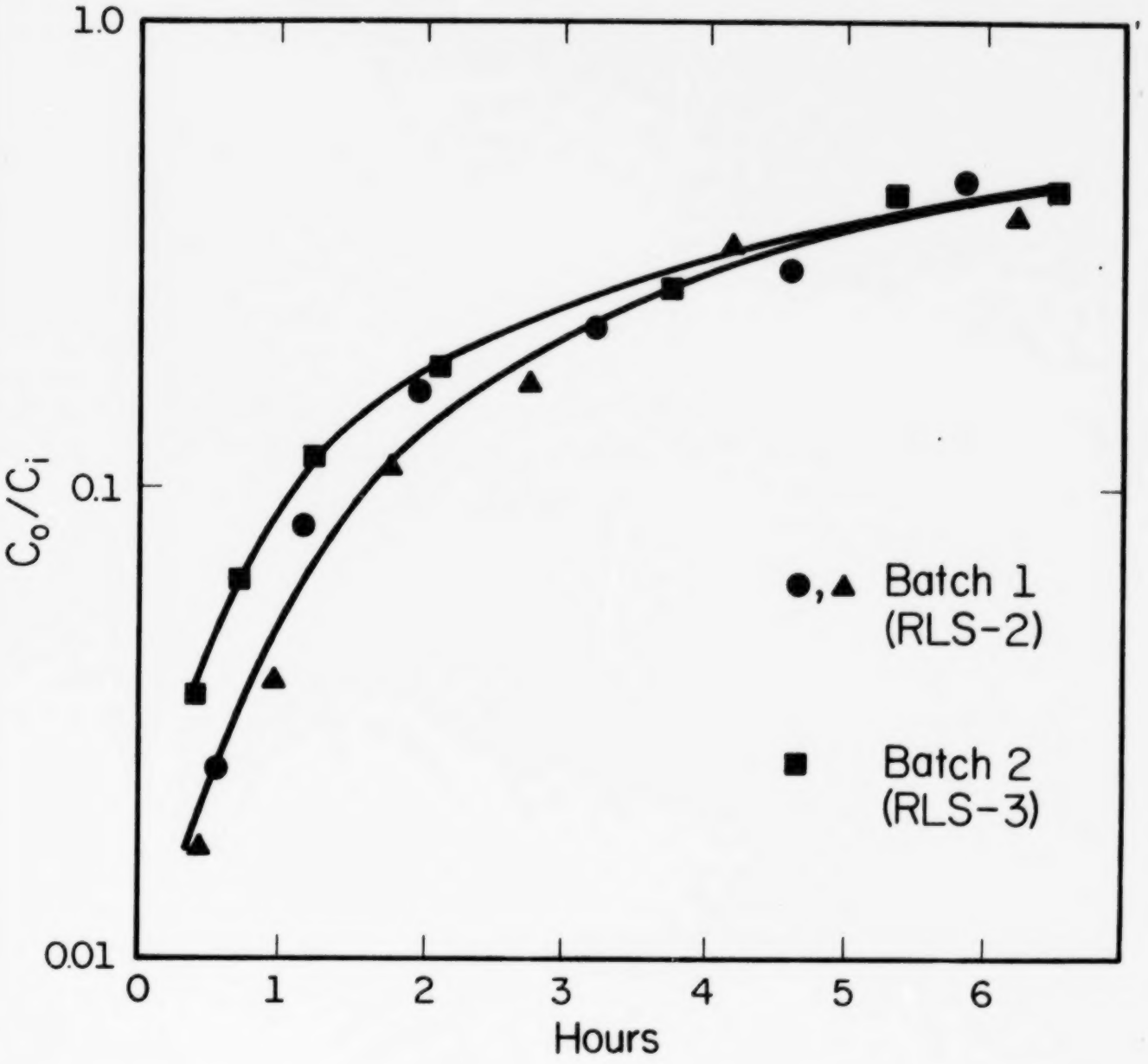


Figure 15 Reproduction of standard preparation - activity vs. time for sawdust

V. CONCLUSIONS

1. Both the efficiency and the capacity of a MnO_2/Sawdust Filter are greatly superior to those of activated carbons for removal of Hydrogen Sulfide from air.

2. For Amines and Mercaptans, activated carbons are better than the form of MnO_2/Sawdust presently available. However, the MnO_2/Sawdust has not yet been optimized for control of these odors.

   For control of odors comprised of a number of pollutants, the combined use of MnO_2/Sawdust and activated carbon would be effective.

VI. RECOMMENDATIONS

The following objectives should be met:

(1) To optimize the efficiency and capacity of MnO_2-sawdust for adsorbing H_2S, mercaptans and amines.

(2) To obtain the necessary data to enable prediction of the performance of full scale MnO_2-sawdust filters in practical air pollution control situations.

(3) To obtain data on the performance of MnO_2-sawdust filters for adsorbing noxious, odorous and corrosive gaseous constituents from selected effluent sources (Viscose, Kraft, Refinery and Sewage effluents).

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VIII. APPENDIX

A. Conversion Factors

		multiply by	
Gas Velocity	ft/min	.5080	cm/s
Temperature	^{o}F	$5/9(^{o}F-32^{o})$	^{o}C
Bed Dimensions	inches	25.40	mm
Pressure	mmHg	1332.	$dynes/cm^2$

Table I

Data for Figure 9

	Preparation 20	Preparation 20A	Preparation 20B	Preparation 20C
Run No.	701	705	704	714
Active Material	8x10 Mesh (Tyler) Sawdust	> 100 Mesh Tyler	> 325 Mesh Tyler	> 325 Mesh Tyler
Ratio Glass/Powder	No Glass	3.5:1.0	3.5:1.0	3.5:1.0
Gas Velocity ft/min	200	44	44	44
H_2S Concentration (ppm)	5.2	97	120	35
Relative Humidity (%)	60%	60%	60%	60%
Pressure Drop Across Bed	43mm H_2O	158mm Hg	417mm Hg	109mm Hg
Amount Mn in Bed (g)	.87	.17	.20	.27
Air Temperature ^{o}F	80	76	74	79
Bed Height	1"	12mm	12mm	12mm
Bed Diameter (mm)	30mm	16mm	16mm	16mm

Table II
Properties of Various Preparations

Sample Preparation	Type	Sample No.	Run No.	Surface Area m^2/g	%K^+ wt	%Na^+ wt	%C wt	%Mn wt	Mn Valence State
Standard Preparation Hemlock 8 x 10	Sawdust	20	701	4.55	9.08	0.70	30.03	13.34	74.7 - 86.2% Mn(IV) 25.3 - 13.8% Mn(III)
	Shakeoff	20A	718	15.98	14.5	0.94	5.53	32.53	86.9 - 99.6% Mn(IV) 13.1 - .37% Mn(III)
	Decant	20B	717	75.45	13.4	0.67	2.06	40.77	73% Mn(IV) 27% Mn(III)
	Extract	20C	714	.58	11.0	4.2	2.11	37.85	86.1% Mn(IV) 13.9% Mn(III)
Hemlock 8 x 10 Standard Preparation except $NaMnO_4$ for $KMnO_4$	Sawdust	21	707	3.77	0.37	6.44	29.03	15.71	74% Mn(IV) 26% Mn(III)
	Shakeoff	21A	715	16.0	0.65	12.9	4.53	38.14	71.4% Mn(IV) 28.6% Mn(III)
	Decant	21B	711	59.8	0.39	9.9	2.10	39.15	83.3% Mn(IV) 16.7% Mn(III)
	Extract	21C	No Data	No Data	0.43	10.7	1.21	40.35	88.2% Mn(IV) 11.8% Mn(III)
Hemlock 8 x 10 Standard Preparation except KOH for NaOH	Sawdust	24	722	4.27	8.42	0.02	29.29	16.39	45.8% Mn(IV) 54.2% Mn(III)
	Shakeoff	24A	725	11.1	17.9	0.1	5.81	35.2	70.1% Mn(IV) 29.9% Mn(III)
	Decant	24B	724	94.8	11.2	0.048	1.64	43.17	74.3% Mn(IV) 25.7% Mn(III)
	Extract	24C	No Data	No Data	No Data	No Data	0.56	42.86	91.0% Mn(IV) 9.0% Mn(III)